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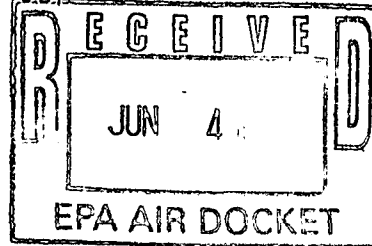
***Docket Number:***

**A-91-46**



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

DEC 12 1991



OFFICE OF  
RESEARCH AND DEVELOPMENT

MEMORANDUM

**SUBJECT:** ORD's Comments on Ethyl Corporation's Resubmittal of a Waiver Application for Methylcyclopentadienyl Manganese Tricarbonyl (MMT)

**FROM:** Peter W. Preuss, Director  
Office of Technology Transfer  
and Regulatory Support (H-8105)

**TO:** Richard Wilson, Director  
Office of Mobile Sources (ANR-455)

This memo transmits the results of ORD's review of Ethyl Corporation's resubmittal, dated July 12, 1991, of a waiver application for the introduction of methylcyclopentadienyl manganese tricarbonyl (MMT) into unleaded gasoline. ORD offices and laboratories participating in this review included the Environmental Criteria and Assessment Office/Research Triangle Park; the Atmospheric Research and Exposure Assessment Laboratory; the Health Effects Research Laboratory; the Environmental Research Laboratory, Athens, Georgia; the Environmental Monitoring Systems Laboratory, Las Vegas, Nevada; and the Office of Health and Environmental Assessment.

In our review, we considered the resubmittal and various other information submitted to the docket; ORD's MMT risk assessment of October 31, 1990; and information obtained in the Mn/MMT Workshop that ORD sponsored in March, 1991. We continue to believe that there are insufficient data available to allow ORD to conclude quantitatively whether the increased use of MMT will (or will not) increase public health risk. Our detailed comments are contained in Attachment A. We will provide recommendations separately on what information is needed to improve the quantitation of the risk assessment.

Please contact me or Stanley Durkee of my staff (260-7891) should you wish to discuss any of these comments.

Attachment

cc: J. Carra, OTS  
M. Smith, OMS  
ORD's MMT Risk Assessment Team

## ATTACHMENT A

### ORD's Comments on Ethyl Corporation's July 12, 1991 Resubmittal of a Waiver Application for the Use of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) IN Unleaded Gasoline

#### SUMMARY

In its October 31, 1990, Comments to OMS on Ethyl's 1990 methylcyclopentadienyl manganese tricarbonyl (MMT) waiver application (ORD, 1990), ORD evaluated potential health and environmental impacts in a number of areas. The most significant issue was associated with the inhalation of manganese (Mn), particularly the fine particulate  $Mn_3O_4$  that results from the combustion of MMT as an additive to gasoline. Because of uncertainties in both the health and exposure assessments, ORD could not determine quantitatively whether the increased use of MMT would (or would not) result in adverse health effects. In addition, ORD concluded there is a potential for human exposure via groundwater contaminated by MMT and exposure to benthic organisms due to releases into surface waters. ORD's analyses also indicated that little risk would occur due to oral exposures resulting from the deposition of Mn-containing particles on surfaces such as soil. Finally, ORD, found that the introduction of MMT could possibly reduce tropospheric ozone, greenhouse gas emissions, and cancer risk, although the degree of benefit in each case is uncertain.

To assist in identifying information needed to improve the quantitation of ORD's MMT risk assessment, ORD sponsored a Mn/MMT Workshop March 12- 15, 1991. Participants included invited scientists from academia, various Federal agencies, Environment Canada, the Ethyl Corporation, and the Environmental Defense Fund. A summary of the workshop discussions was provided to each participant (ORD, 1991).

Based on ORD's review of Ethyl Corporation's resubmitted waiver application of July 12, 1991, ORD continues to believe that it is not possible, based on existing data, to conclude quantitatively whether the increased use of MMT will (or will not) increase public health risk. With regard to the Mn assessment, ORD used new exposure information provided by Ethyl Corporation to revise its 1990 Mn exposure estimate resulting in a lower value. Also, ORD carefully evaluated Ethyl

Corporation's arguments that the Mn Inhalation Reference Concentration (RfC) used as part of the health assessment should be higher, but decided not to change its assessment. In fact, based on production data submitted, ORD's concern about using the Mn RfC to interpret the potential risk from  $Mn_3O_4$  is increased.

With regard to other issues posed by the resubmittal, ORD determined, as a result of information presented at the March, 1991 Mn/MMT Workshop, that neither pure MMT nor  $Mn_3O_4$  poses a human health risk via potable water ingestion due to ground or surface water contamination. However, ORD did find that because information on spills and leaks was not provided, it continues to be not possible to conduct an assessment of whether spills/leaks of pure MMT to waters could affect exposures to benthic organisms. Also, ORD evaluated Ethyl Corporation's analysis indicating that MMT use would avoid 48 cancer cases/year (relative to conventional fuel) and concluded that the emission data underlying the analysis were too sparse to warrant confidently drawing this conclusion. Finally, ORD evaluated Ethyl Corporation's analysis showing that the photochemical reactivity of emitted hydrocarbons decreases 28 percent with MMT use; and ORD determined that the emissions data base was too uncertain to warrant concluding as much of a decrease as Ethyl Corporation asserted.

#### I. COMMENTS ON HEALTH RISK ASSESSMENT FOR MANGANESE (Mn)

##### Comments on Mn Health Assessment Issues Raised by Ethyl

The Ethyl resubmittal presented no new health studies that ORD had not already considered. However, Ethyl Corporation raised two major comments concerning EPA's judgments of existing data with regard to the Mn RfC. (An RfC is defined as an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily inhalation exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime.)

First, Ethyl argued that the RfC was set too low, because EPA had inappropriately applied a modifying factor of 3 to account for EPA's judgment that there was an overestimate of exposure in the published occupational study (Roels et al., 1987) that served as the principal study for the RfC. Ethyl Corporation argued that this factor should not be applied, since exposure had not increased during the study, as evidenced by letters from F. Delloye and M. Fautsch of SEDEMA, the operator of the facility in which the Roels study was conducted, and one of the co-authors of the Roels et al. study, Dr. Robert Lauwerys. According to these letters, the area of the plant and the number of workers expanded with time, but no data were presented to enable calculation of revised exposures. ORD believes there is insufficient information in the letters to justify changing the occupational exposure

modifying factor of the RfC.

Ethyl argued that the uncertainty surrounding the RfC is less than an order of magnitude because the studies used were epidemiological studies, and, therefore, the RfC should be rated with a "high" level of confidence. ORD maintains that a "medium" level of confidence to the RfC is appropriate, based upon criteria described in the Inhalation Reference Concentration Methodology Document (U.S. EPA, 1990). ORD maintains that, regardless of the category of confidence, the RfC by definition represents an estimate with no greater precision than an order of magnitude.

However, additional information, provided by SEDEMA, suggests that the relevance of the Mn RfC to  $Mn_3O_4$  may be even more questionable than was previously recognized by ORD. This information showed that while production levels in the key RfC occupational study did include Mn oxides and salts,  $Mn_3O_4$  production was a small fraction of the total. Indeed, for all years preceding 1985, the indicated quantities of  $Mn_3O_4$  are so small in relation to the other Mn compounds that amounts of  $Mn_3O_4$  cannot be estimated. As discussed in ORD's 1990 Mn risk assessment (ORD, 1990), since different species of Mn have unquantified differences in toxicity, ORD remains concerned about the use of an RfC for Mn to interpret the risk from  $Mn_3O_4$ .

Finally, ORD notes that the resubmittal contains a paper by Dr. Hochberg explaining that manganese exposure (and manganism) is not related to idiopathic parkinsonism. While ORD has not subjected Dr. Hochberg's paper to peer-review, it generally has no major objections to the conclusion that Mn toxicity and Parkinsonism are different diseases. This, however, is irrelevant to ORD's risk characterization, because the risk characterization was based on signs and symptoms of neurotoxicity in Mn-exposed workers, not on Parkinsonism.

Therefore, ORD concludes the information in the resubmittal is insufficient to justify changing its October 31, 1990, health assessment, based on the Mn RfC. However, ORD's concern about the use of an RfC based on exposure to Mn oxides and salts to interpret the potential risk from  $Mn_3O_4$  is increased.

#### Comments on Mn Exposure Assessment Issues Raised by Ethyl Corporation

The resubmittal did provide new exposure information, including the results from a field measurement program of personal exposures (of office workers and taxicab drivers) to airborne Mn in Toronto, Canada, where MMT is used as an additive in gasoline. The sampling was conducted for a two-week period (from February 4, 1991, to February 19, 1991), and personal exposure times were approximately 7 days in most cases. The individuals monitored were instructed to

carry the samplers with them when outdoors and to keep them nearby when indoors. The reported average concentration of MMT in the gasoline in Toronto during this period was 0.039 g/gal, or 1/26th g/gal, which is only slightly greater than the amount requested by Ethyl Corporation for use in U.S. unleaded gasoline, namely 0.03125 g/gal, or 1/32nd g/gal.

The Toronto field measurements indicated that for seventeen office workers, the mean exposure to airborne Mn was  $0.013 \mu\text{g}/\text{m}^3$ . For these office workers, the highest Mn exposure was  $0.048 \mu\text{g}/\text{m}^3$  (one week averaging period). The second highest Mn exposure was  $0.046 \mu\text{g}/\text{m}^3$ ; the third highest,  $0.027 \mu\text{g}/\text{m}^3$ . The lowest exposure was  $0.002 \mu\text{g}/\text{m}^3$ .

Taxicab drivers in Toronto had generally higher exposures to Mn than office workers. Six taxicab drivers were studied for two weeks, yielding 10 one-week average concentrations, with a mean of  $0.035 \mu\text{g}/\text{m}^3$ . These personal exposure measurements ranged from  $0.015 \mu\text{g}/\text{m}^3$  to  $0.049 \mu\text{g}/\text{m}^3$ . Thus, the average exposure of taxicab drivers was 2.7 times higher than the average exposures of the office workers in Toronto.

In addition to the personal monitoring data, Ethyl presented:

- results of modeled exposures, using the South Coast Risk Exposure and Assessment Model (SCREAM) and Lead Ratio Models;
- exposure estimates using ORD's 1990 estimated median Mn average exposures, but using the distribution of exposures from the Azar et al. (1975) personal monitoring study of lead exposures in place of the carbon monoxide distribution for peak exposures ORD had used;
- four measurements of Mn concentrations in two Toronto microenvironments, an underground parking garage ( $0.41 \mu\text{g}/\text{m}^3$  and  $0.093 \mu\text{g}/\text{m}^3$ ) and a hotel motor court ( $0.325 \mu\text{g}/\text{m}^3$  and  $0.231 \mu\text{g}/\text{m}^3$ ). These data, which are 3 to 13 times higher than the average personal exposures of taxicab drivers ( $0.035 \mu\text{g}/\text{m}^3$ ) and 7- 30 times higher than the average personal exposures of office workers in Toronto ( $0.013 \mu\text{g}/\text{m}^3$ ), illustrate the wide distribution of Mn exposures within microenvironments that would be expected.

ORD believes the Toronto personal monitoring study provides the best available data and, therefore, used these data in developing a revised exposure estimate. ORD then compared this estimate to both ORD's original 1990 exposure estimates (ORD, 1990) and those submitted by Ethyl Corporation.

ORD has confidence in the usefulness of the Toronto data. Ethyl's application

included the results of the 3-week personal monitoring lead (Pb) study (Azar et al., 1972), taken when all U.S. gasoline contained Pb. That study included measurements of lead exposures to taxicab drivers and office workers in Los Angeles and taxicab drivers in Philadelphia. ORD performed a statistical analysis on the data that suggests that the two-week Mn exposure data and the 3-week lead exposure data have similarities. (For example, the average exposure for the taxicab drivers in the Azar study ( $6.10 \mu\text{g}/\text{m}^3$  Pb) was 1.99 times greater than the average office worker exposure ( $3.06 \mu\text{g}/\text{m}^3$  Pb), while in the Toronto study the average ( $0.035 \mu\text{g}/\text{m}^3$  Mn) was 2.69 times greater than the average office worker exposure.)

ORD performed a three-step analysis to develop the revised exposure assessment:

First, ORD assumed that the air Mn level of  $0.035 \mu\text{g}/\text{m}^3$ , the reported mean exposure level of the taxicab drivers (one week average), represented the mean of the highest exposure distribution of people in Toronto.

Second, using the results of the probability-based Denver-Washington D.C. carbon monoxide study of personal exposures (Johnson, 1984 and Johnson et al, 1986), ORD assumed that 4 percent of the exposed urban population in any city with similar MMT content in the gasoline would be in the high exposure cluster and would be at, or above, the Mn level of  $0.035 \mu\text{g}/\text{m}^3$ . (In the carbon monoxide study, it had been determined that about 4 percent (i.e., 29 out of the representative sample of 712 persons) formed a high exposure cluster consisting largely of persons in close proximity to motor vehicles, such as policemen, crane operators, taxicab drivers and a few members of the general public.)

Finally, ORD estimated that the annual mean air Mn exposure of this high exposure cluster of people to be  $0.09 \mu\text{g}/\text{m}^3$ . This number represents the 96th percentile exposure to Mn, with an undetermined amount of uncertainty. This estimate was made to account for the difference in Mn background between the reported results of the personal monitoring study, which ranged from 0.002 to  $0.049 \mu\text{g}/\text{m}^3$ , and those of annual average ambient Mn concentration levels, reported by Ethyl Corporation, in downtown Toronto, which ranged from  $0.025 \mu\text{g}/\text{m}^3$  to  $0.055 \mu\text{g}/\text{m}^3$  (derived from monitoring sites for 1985 through 1988). The difference in the lowest personal exposure value and the ambient values suggest one of the following: the concept of a fixed background for all microenvironments is not realistic for Mn; the background Mn level for this particular two-week period was on the order of  $0.002 \mu\text{g}/\text{m}^3$ ; or the particulate matter samples in the personal monitoring and ambient data are different in size. Assuming that background for some years could be as high as the highest Toronto background ambient level of  $0.055 \mu\text{g}/\text{m}^3$ , the value of  $0.055 \mu\text{g}/\text{m}^3$  was added to  $0.035 \mu\text{g}/\text{m}^3$  to yield the estimate of  $0.09 \mu\text{g}/\text{m}^3$  for the high exposure cluster. Lacking concurrent Mn background data, ORD has assigned this particular background value even though it is

unknown whether the Mn particles from the Toronto personal monitoring study are comparable in size to those reported in the Toronto ambient monitoring data. (Also, ORD notes that Ethyl Corporation's resubmittal also contains information showing higher ambient values for Ontario for the years 1982 through 1985, using data from the same source, the Ontario Ministry of the Environment. While these values appear to reflect increases in ambient levels, more information is needed to interpret these data and their bearing on the 1985-1988 data.)

ORD then compared its revised 96th percentile estimate of  $0.09 \mu\text{g}/\text{m}^3$  to estimates in the previous ORD exposure assessment (ORD, 1990). As shown in Figure 1, ORD's revised estimate is lower, but on the same order as ORD's original estimate ( $0.41 \mu\text{g}/\text{m}^3$ ), which assumed 30 percent of the Mn is emitted at the tailpipe. (Ethyl Corporation considers thirty percent Mn emissions to be the plausible upper bound; ORD believes this value reflects the average emissions to be expected over time from a wide mix of vehicles.) The revised ORD estimate is similar to Ethyl Corporation's exposure estimates of 99th percentile values (ranging from  $0.07 \mu\text{g}/\text{m}^3$  to  $0.14 \mu\text{g}/\text{m}^3$  Mn), based on field studies of personal lead exposures conducted by Azar et al. (1975). Also, the revised estimate is similar to Ethyl Corporation's modeled estimate of the "maximum" exposure ( $0.2 \mu\text{g}/\text{m}^3$  Mn), assuming 30 percent emissions, using SCREAM.

There are considerable uncertainties in all Mn exposure estimates. Even though ORD believes the Toronto personal monitoring study provides the best available Mn exposure information, there are major uncertainties associated with the revised ORD estimate:

- the sample size was very small and was not statistically derived; therefore, it is uncertain whether the samples represent the subgroups adequately and whether the Toronto population subgroups represent the overall population of Toronto adequately;
- the sampling period was only for two weeks in February, 1991, and, therefore, it is uncertain whether the sample represents the rest of the year, or other years, in terms of such variables as the Mn concentration in gasoline, human activity patterns, traffic volume and flow (as related to human activities and exposures), the Mn emission rate from typical mixes of vehicles (as opposed to well-tuned test vehicles) and meteorology;
- it is uncertain what portion of the total Mn is contributed by vehicles as opposed to stationary or other sources;
- the percentage of vehicles in Toronto actually using MMT in their gasoline is unknown.

- it is uncertain whether the Mn exposures experienced in Toronto are representative of those that might be experienced in other Canadian cities, or within other cities of the United States.
- it is uncertain whether Mn exposure distributions are analogous to those in probability-based, historical carbon monoxide exposure studies.
- the background value that ORD used in developing its estimate is uncertain because it is unknown whether the Mn particles from the Toronto personal monitoring study are comparable in size to those reported in the Toronto ambient monitoring data.

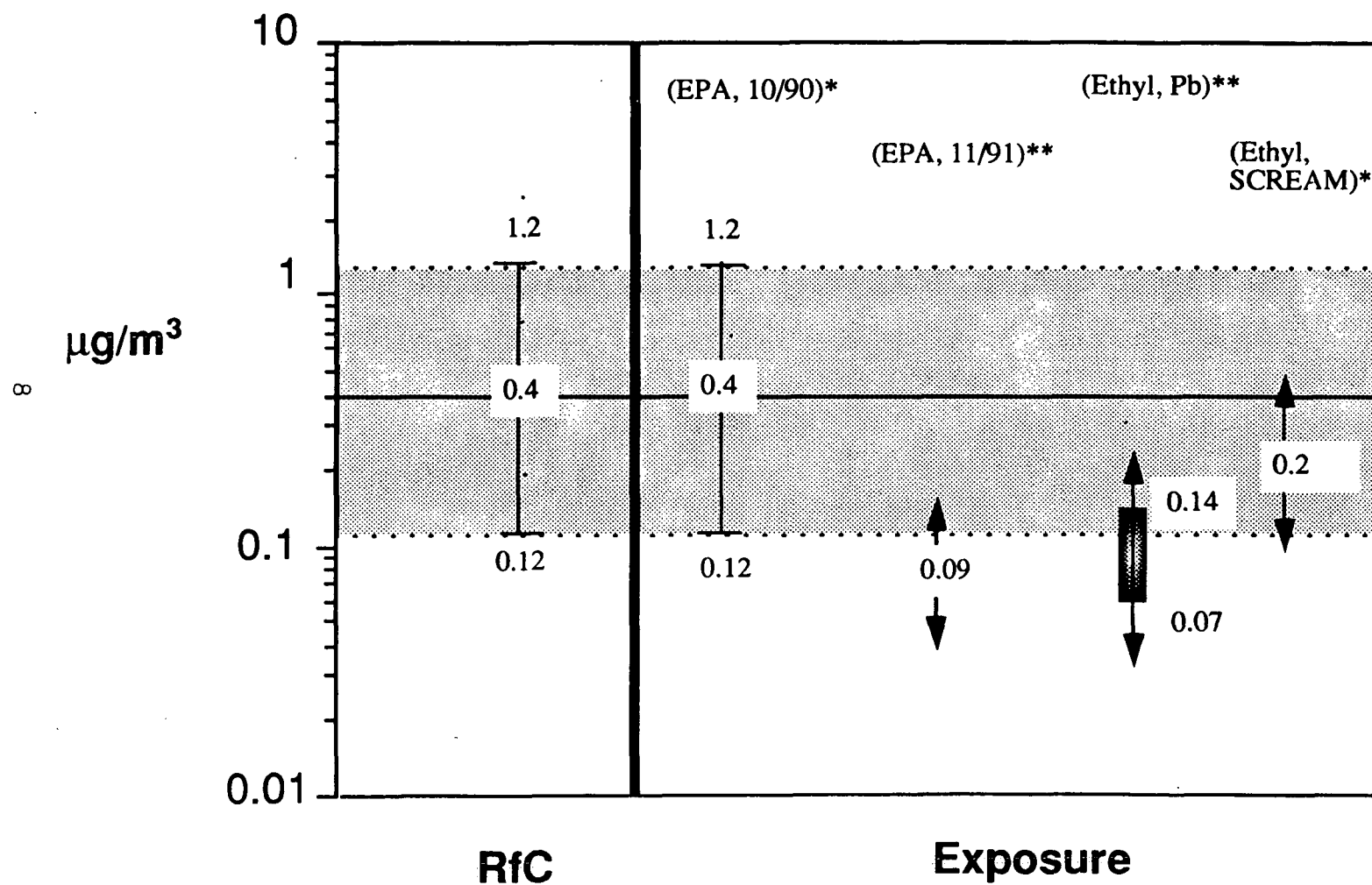
#### ORD's Revised Mn Risk Characterization

The risk characterization is depicted on Figure 1. As shown, the RfC for Mn is compared to ORD's original exposure estimate, ORD's revised exposure estimate, and Ethyl Corporation's exposure estimates.

As depicted, although the revised ORD exposure estimate is about a factor of 4 below the RfC, the uncertainty in both the exposure and RfC estimates may overlap. In addition, other concerns make it difficult to conclude that MMT is or is not likely to increase public health risks. The RfC methodology uses a set of generic uncertainty factors to account for the uncertainties involved, e.g., in extrapolating from data on healthy adult male workers to possibly much more susceptible subpopulations such as children, or in extrapolating from effects observed under subchronic exposure conditions to chronic (lifetime) exposure effects. However, such factors are not necessarily accurate and do not necessarily account for all of the uncertainties associated with a particular chemical. For example, the standard RfC uncertainty factors are not meant to address the possibility that Mn exposure could result in a delayed or long-latency form of neurotoxicity, which might not be evident until rather late in life. Furthermore, since different metal species can have different toxicological potencies, the adequacy of using the Mn RfC (based on exposure to mixed Mn oxides and salts) to predict the potential risks associated with  $Mn_3O_4$  exposures remains an important issue.

Therefore, ORD continues to believe that it is not possible to conclude definitely whether the increased use of MMT in unleaded gasoline will (or will not) increase public health risk.

# Figure 1. RfC and Exposure Estimates



\* Modeled estimate assuming 30% tailpipe Mn emissions.

\*\* Estimate derived from personal exposure monitoring.

## II. COMMENTS ON ENVIRONMENTAL HAZARD WITH MMT

Based on information presented at the Mn/MMT Workshop (ORD, 1991), ORD determined that neither pure MMT nor  $Mn_3O_4$  posed a threat to human health via groundwater contamination. However, Ethyl Corporation's resubmittal did not provide exposure information, specifically spill-frequency volume release data applicable to MMT, needed to assess whether spills/leaks of pure MMT into sensitive freshwater or marine ecosystems could affect exposure to benthic organisms. As indicated in ORD's previous comments to OMS on Ethyl Corporation's waiver application (ORD, 1990), in its pure state, MMT spilled or leaked into surface water would settle directly to the bottom and partition between water and the sediment. In the absence of light, its half life is longer than two months. As indicated previously, however, since it can be expected that there will be very few sites where large volumes of MMT are produced and stored, the populations exposed will likely be limited.

## III. COMMENTS ON CANCER RISK ASSESSMENT FOR MMT-CONTAINING GASOLINE

Ethyl Corporation's resubmitted waiver application contained an analysis of cancer incidence which indicated that an avoidance of 48 cancers/year relative to conventional gasoline could be achieved by using MMT. ORD found that the estimate was based on toxic hydrocarbon emission speciation data from only two data points associated with two 1988 Ford Crown Victoria test vehicles from Ethyl Corporation's 48-vehicle test fleet. Each vehicle had a mileage of approximately 67,000 miles. Only one test vehicle was actually tested with MMT added to unleaded gasoline; the other vehicle was tested with neat fuel or with neat fuel to which xylenes had been added (for octane enhancement), so that comparisons of emissions between the two vehicles could be made on an "equal octane" basis. ORD believes these data are too sparse to form the basis of an estimate of cancer reduction with the use of MMT.

## IV. COMMENTS ON OTHER ENVIRONMENTAL ISSUES

### A. Effects on Tropospheric Ozone

ORD concluded in its earlier MMT assessment (ORD, 1990) that MMT in gasoline would be very unlikely to have a significant adverse effect on ozone formation, and that the presence of MMT as a substitute for xylenes may actually result in decreases in photochemical ozone in specific cases. However, ORD noted

that xylenes are known to be photochemically reactive and that if other octane enhancers had been used in the analysis, the relative benefit, if any, of MMT on ozone formation would be reduced.

In its resubmittal, Ethyl Corporation estimates that the photochemical reactivity of emitted hydrocarbons decreases 28 percent with MMT use. ORD believes this estimate is uncertain, because it is based on the same limited two-vehicle emission data base used in estimating cancer reductions (see part III above). Also, the comparisons are made with non-MMT vehicles using aromatics for octane enhancement (i.e., xylenes), that typically increase tailpipe hydrocarbon (HC) emissions. For this reason, the difference in the speciated HC results is likely to be greater than if other non-aromatic octane enhancers were used that are less-photochemically reactive, such as MTBE.

#### **B. Effects on Greenhouse Gas Inventory**

In its earlier comments to OMS (ORD, 1990), ORD performed an analysis that concluded that the introduction of MMT would result in negligible changes to the greenhouse gas inventory. ORD has seen no data in the resubmittal to cause it to change this assessment.

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